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Tour, J. M.; John, J. A.

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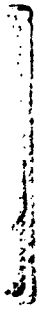

Department of Chemistry and Biochemistry
University of South Carolina
Columbia, SC 29208

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Columbia, SC 29208

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13. ABSTRACT (*Maximum 200 words*)

Described is the synthesis of polyphenylenes via the Bergman cyclization of enediyne monomers. These monomers were synthesized via the Stephans-Castro/Sonogashira reaction and polymerized under varying conditions.

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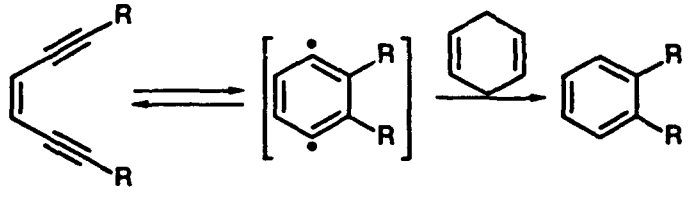
Synthesis of Polyphenylenes via Bergman Cyclization and Polymerization of Enediyne Monomers

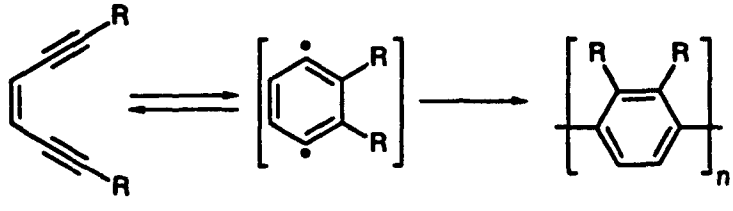
James M. Tour* and Jens A. John
Department of Chemistry and Biochemistry
University of South Carolina
Columbia, South Carolina 29208

In the early 1980s Bergman's study of thermal cycloaromatization of enediynes led to the suggestion of a 1,4-benzene diradical as an intermediate.[1] Later, DNA-cleaving antibiotics such as the esperamicins, calicheamicins and dynemicins were discovered to possess a cyclic enediyne moiety which underwent a Bergman cyclization upon activation.[2] Therefore synthetic and mechanistic studies were performed to investigate this reaction further by thermally cyclizing a wide variety of enediynes in the presence of 1,4-cyclohexadiene as a radical quencher.[1,3]

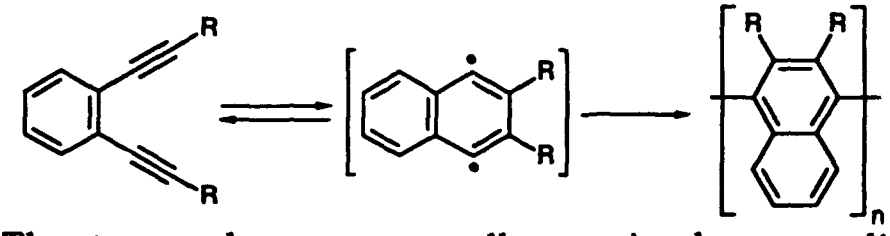


Since the natural products contained cyclic enediynes, most of the studies focused on these compounds. The model cyclizations in the presence of 1,4-cyclohexadiene resulted in moderate yields of substituted benzenes and polymeric by-products.

Our interest in the area was kindled when we regarded the intermediate 1,4-benzene diradical as a building block for substituted polyphenylenes.



In addition, benzene analogs of enediynes were envisioned to form 1,4-naphthalene diradical intermediates which in turn could lead to naphthalene-based polymers.

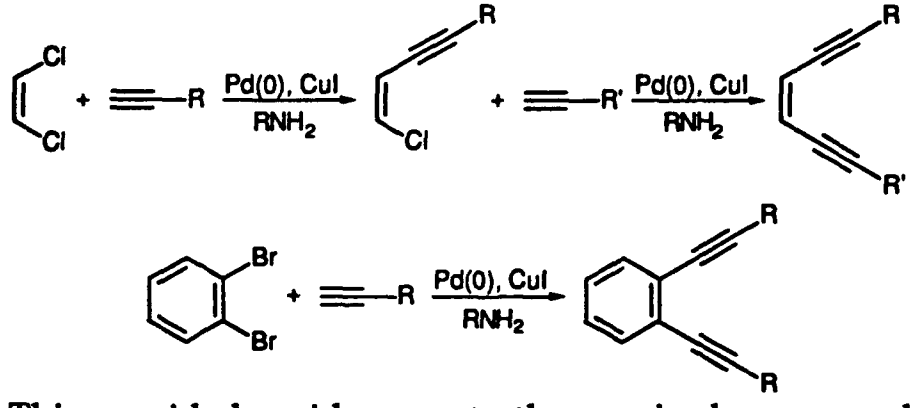


The targeted monomers all contained non-cyclic enediynes to ensure better stability and ease of synthesis.

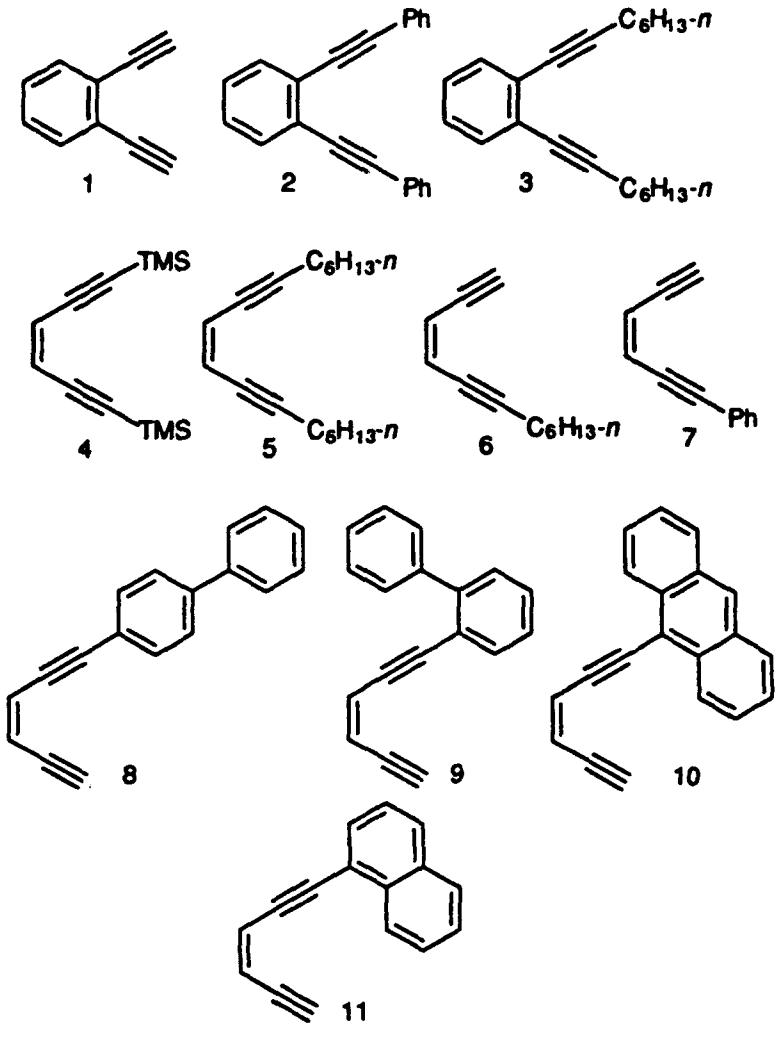
Recently, Swager *et al.* used cyclic benzene analogs of enediynes to construct an all carbon ladder polymer.[4]

Synthesis of Enediyne Monomers

Both alkenyl and aryldiyne monomers were synthesized via the Stephans-Castro/Sonogashira reaction[5] in which a vinyl or aryl halide was coupled with a terminal acetylene.



This provided rapid access to the required mono- and disubstituted alkynyl and aryl diyne monomers. A list of the monomers prepared is shown below.



These monomers were then polymerized under various conditions (Table I).

Table I.

Monomer	Method[a]/ Temp.	Mw	Mn	$\frac{M_w}{M_n}$	solubility
1	A/170	-	-	-	insoluble
2	A/400	245	141	1.7	0.33 sol. 0.67 insol.
3	A/340	106	71	1.5	0.5 sol. 0.5 insol.
4	A/300	2850	1040	2.7	soluble
5	A/300	590	430	1.4	soluble

4	B/120	325	312	1.0 4	soluble
5	B/140	1880	790	2.4	soluble
6	B/120	3930	1570	2.5	soluble
5	D/150	915	522	1.7	soluble
7	B/150	305000	9500	32	soluble
7	C/140	2000	630	3.2	soluble
7	A/150	2000	630	3.2	soluble
7	E/47 to 118	3200	940	3.4	soluble
8	B/ 95	10600	4100	2.6	soluble

[a]Method A: heated neat. Method B: heated in benzene. Method C: added slowly to refluxing 1,2-dichlorobenzene. Method D: heated together with a radical initiator. Method E: slowly increased temperature over several hours.

Discussion

These results led to several conclusions. First, the use of benzenoid monomers was not efficacious due to the lack of polymer solubility, low molecular weights and high polymerization temperatures required. Secondly, alkyl substituents in the monomer led to low molecular weights presumably due to radical transfer generating more stable alkyl, allylic, or benzylic radicals and ultimately causing premature chain termination. Last, substitution on both alkynes required higher polymerization temperatures. At these temperatures, decomposition of the monomer may compete with polymer growth. The best results were obtained when one of the alkynes was unsubstituted and the other one was bearing an aromatic group.

Conclusion

This study has shown the feasibility of the polymerization of enediyne monomers via a Bergman cyclization to afford low molecular weight polyaromatics. Our results show that soluble polyphenylenes can be easily made from non-cyclic enediynes. Further studies with other aryl substituents are planned to narrow the polydispersity and increase the molecular weight.

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